GENERAL ATOMIC
DIVISION OF GENERAL DYNAMICS

GA-7324

EFFECTS OF ADDITIONS OF NON-METALLICS ON THE PROPERTIES OF VAPOR-DEPOSITED TUNGSTEN*

by

J. Chin, A. F. Weinberg, and J. R. Lindgren

This ~~paper was~~ presented at the Houston Thermionic Conversion Specialist Conference
Houston, Texas
(November 2, 3, 4, 1966)

*This work was supported by the National Aeronautics and Space Administration under Contract NAS 3-6471.

GENERAL ATOMIC

DIVISION OF

GENERAL DYNAMICS

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

GA-7324

Copy No.

EFFECTS OF ADDITIONS OF NON-METALLICS ON THE PROPERTIES OF VAPOR-DEPOSITED TUNGSTEN*

by

J. Chin, A. F. Weinberg, and J. R. Lindgren

This paper was presented at the Houston Thermionic Conversion Specialist Conference
Houston, Texas
November 2, 3, 4, 1966

*This work was supported by the National Aeronautics and Space Administration under Contract NAS 3-6471.

ABSTRACT

A study was conducted to determine the change in selected properties from base line characteristics of vapor-deposited tungsten as trace quantities of non-metallics were introduced. The addition of carbon, nitrogen or oxygen raised the low temperature yield strengths without raising the ductile-to-brittle transition temperature above 200°C. Yield strengths at 1800°C of specimens containing these additives were also higher than specimens without this intentional addition. Hardness and ductile-to-brittle transition temperatures were not systematically affected by changes in the fluorine content while grain boundary porosity was affected.

Thermal treatments of base line specimens of 1800°C to 2500°C reduced the scatter in hardness and ductile-to-brittle transition temperatures. Creep behavior of base line specimens held at 1760°C is reported.

INTRODUCTION

This study was aimed toward greater control of the properties of the tungsten through alterations in its deposition, composition, and thermal treatment. The investigation fell into two broad areas: the influence of additives and a better understanding of tungsten's physical metallurgy.

The studies of additives had two goals: (1) to stabilize the compatibility of tungsten with various nuclear fuels by presaturation of the tungsten with components of the nuclear fuel, instead of forcing the tungsten to extract these components from the fuel itself in an attempt to attain equilibrium; and (2) to favorably influence the mechanical properties, i.e., high-temperature strength or the ductile-to-brittle transition temperature by suitably changing the composition.

An important part of the studies was the defining, by means of statistical limits determined from a large number of identical deposition runs, the normal scatter in chemical composition, physical properties, and mechanical properties which one might encounter in tungsten with no intentional additives. This was necessary to ensure that any changes effected by the additives were significant, in a statistical sense.

Included in the physical metallurgy studies were: (1) the influence of post-deposition thermal treatment on mechanical properties of interest; (2) the influence of cyclic thermal treatments on grain growth, i.e., a high temperature to initiate grain growth (simulating a reactor transient) and a longer holding period at a lower temperature; (3) the influence of low-temperature mechanical strain on subsequent grain growth behavior; (4) long-time high-temperature creep properties.

BASE-LINE DATA EVALUATIONS

The goal of the base line data determination was to establish the reproducibility of vapor-deposited tungsten with regard to the following properties:

a. Impurity content
b. As-deposited microstructure
c. Resistance to grain growth during thermal treatments

d. Ductile-to-brittle transition temperature

e. Bend tests

f. Microhardness

A basic part of the program was, therefore, the fabrication and evaluation of a sufficient number of samples, made under a set of reference conditions, to enable the placement of statistical limits on the selected properties.

The base line process parameters kept fixed for this study were:

a. The deposition temperature was 540° ± 10°C

b. The WF_6-to-H_2 ratio was 1:5 (by volume)

c. The total chamber pressure was 15 ± 5 in. Hg

d. The total gas flow was 2500 ± 50 cm^3/min.

The base line properties, measured from rectangular strips cut from vapor-deposited samples can be summarized as follows, with all values given for a 95% confidence limit:

Impurity Content:	Carbon:	15.5 ± 9 ppm
	Oxygen:	8.7 ± 8.4 ppm
	Fluorine:	46 ± 35 ppm*

Nitrogen and hydrogen not detected at levels above 4 ppm and generally below 1 ppm. Metallic impurities were, in general, below the detectable limit of emission spectroscopy.

DUCTILE-TO-BRITTLE TRANSITION TEMPERATURE (DBTT)

The apparatus used to make the DBTT measurements on vapor-deposited tungsten specimens is shown in Fig. 1. This testing device was designed so that six test specimens could be accommodated during each loading. The

*The fluorine contents reported are from deposits made early in the program from two bottles of WF_6. Fluorine contents of deposits made later in the program from two other bottles of WF_6 supplied by the same vendor and two bottles from ORNL were less than 22 ppm. The fluorine impurity level of the sample was found to be strongly influenced by which bottle of WF_6 is used and how many depositions have been made from that bottle. It, therefore, appears as if the fluorine data reported are representative of the worst WF_6 bottles we have encountered; and, if one collects the data from the last 12 runs, the fluorine content is 15 + 18 - 15 ppm for a 95% confidence limit.

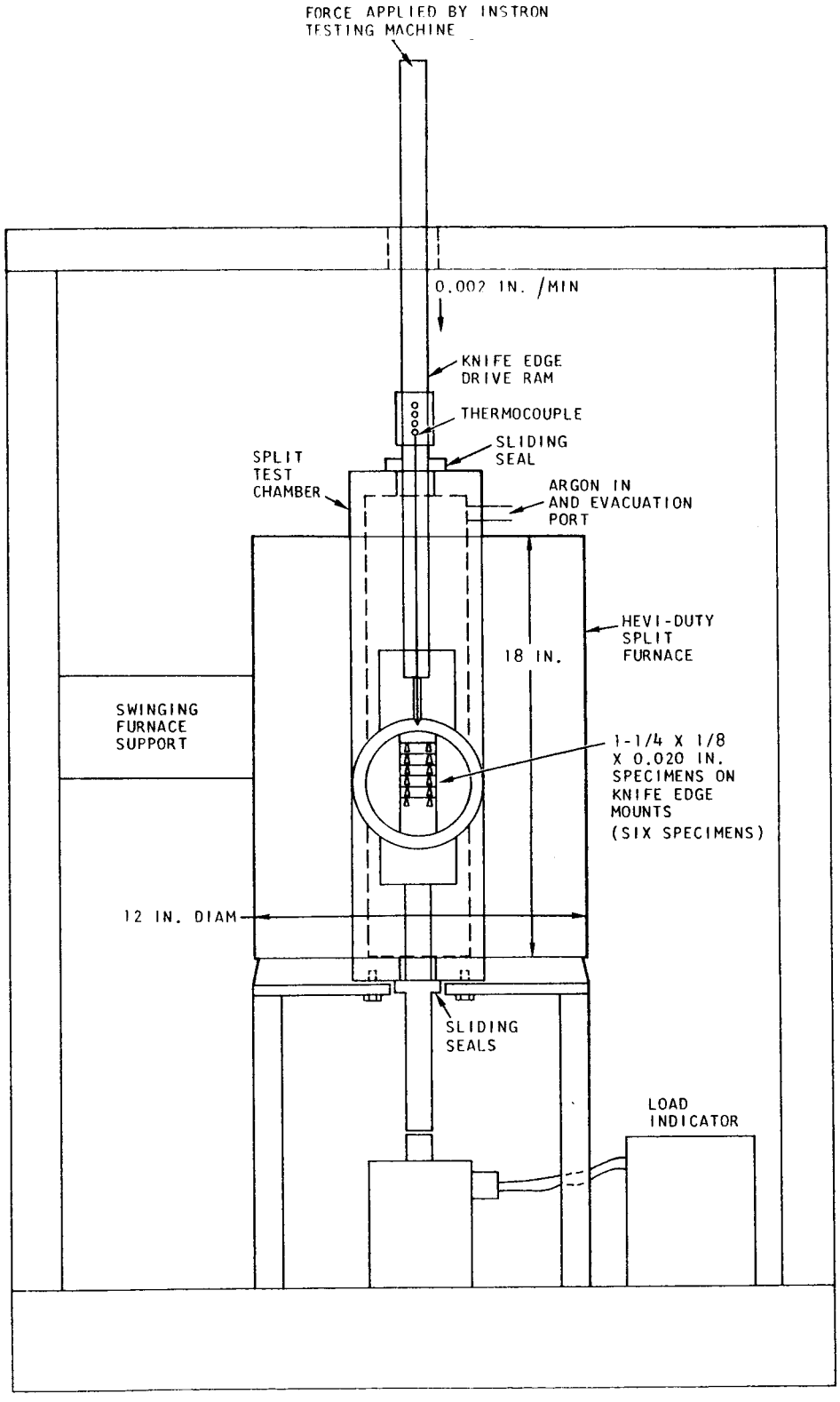


Fig. 1--Schematic of apparatus used to make DBTT tests

chamber containing the specimen holder was evacuated and backfilled with helium prior to specimen testing. Transition temperatures were determined by three-point loading. Specimens were considered ductile when they exhibited any easily discerned plastic deformation prior to fracture. All specimens were stress relieved by slowly heating to 1800°C and holding at 1800°C for 1 hour before DBTT testing. The DBTT(s) measured were 120° ± 41°C.

YIELD STRENGTH MEASUREMENTS

Yield strength measurements at the DBTT were determined with the same apparatus used for DBTT measurements. The yield strengths measured under these conditions were 80,000 ± 30,400 psi.

Yield strength measurements on vapor-deposited tungsten at 1800°C were determined by four point loading. The apparatus consists of a tantalum resistance-heated vacuum furnace equipped with tungsten specimen supports and loading columns tipped with tantalum carbide. The yield strengths reported were the stresses at which measureable (~ 0.2%) plastic yielding occurred.

Yield strengths at 1800°C ranged from 4280 to 4760 psi, with an average value of 4520 psi.

HARDNESS

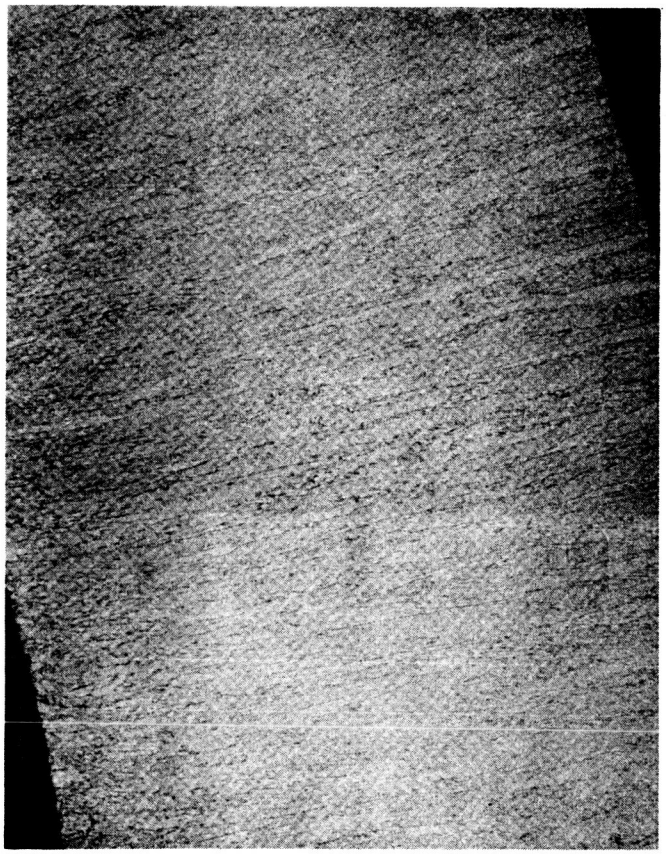
The microhardness, as determined with a 100g load, averaged 422 DPH ± 82 DPH. The hardness does not appear to be related to the contaminant level, DBTT, or grain width.

Grain Width: The grain width was $1.9 \pm 1.1 \times 10^{-2}$ mm.

RESISTANCE TO GRAIN GROWTH

All specimens were resistant to grain growth at 2500°C, after the inner layer of randomly oriented grains had been removed. This verified results of previous experiments.[1]

Fig. 2 shows a typical vapor-deposited tungsten microstructure, preparedunder conditions used to measure the base line properties.



M11962-2 (100X)

Fig. 2--Microstructure of a typical vapor-deposited tungsten specimen prepared under reference condition

ADDITIVES

The additions of carbon, oxygen, and nitrogen were made both by gas-metal reactions and during deposition, in order to separate those effects due to method of addition from those due to quantity of addition. The ranges of additive concentrations obtained were: carbon--24 to 320 ppm; nitrogen--15 to 101 ppm; oxygen--4 to 66 ppm; and fluorine--4 to 96 ppm. The influence of these additives was:

1. Carbon. The behavior of vapor-deposited tungsten to which carbon had been added is shown in Figs. 3 through 6.

   Carbon raised the low-temperature yield strength as high as 200,000 psi, while at the same time not raising the DBTT above 200°C. The yield strength at 1800°C was raised to 7000 to 9000 psi from the ~ 5000 psi observed in low-carbon specimens. Photo-micrographs of carbon containing tungsten deposits are shown in Fig. 7.

2. Nitrogen and Oxygen. The influence of nitrogen and oxygen on the properties and structure of vapor-deposited tungsten were essentially that of a similar amount of carbon. Oxygen did appear to have a lesser effect on the high and low temperature yield strengths.

3. Fluorine. One of the questions about the use of vapor-deposited tungsten which has caused concern is the effect of fluorine as an impurity. At its best, tungsten deposited from WF_6 has been found to contain approximately 4 ppm fluorine, which is roughly the same level found in powder metallurgy tungsten.[2] However, fluorine contents greater than 60 ppm are not uncommon.

   The influence of fluorine content was studied by selecting specimens with a range of fluorine contents from available specimens. It was found that:

   a. Hardness: (1) hardness is not closely related to the fluorine content of the specimens studied after a reference 1800°C thermal treatment; see Fig. 8, and (2) even at a constant fluorine content, thermal treatments which do not affect the gross structure or the purity of the material can cause large changes in hardness as shown in Fig. 9.

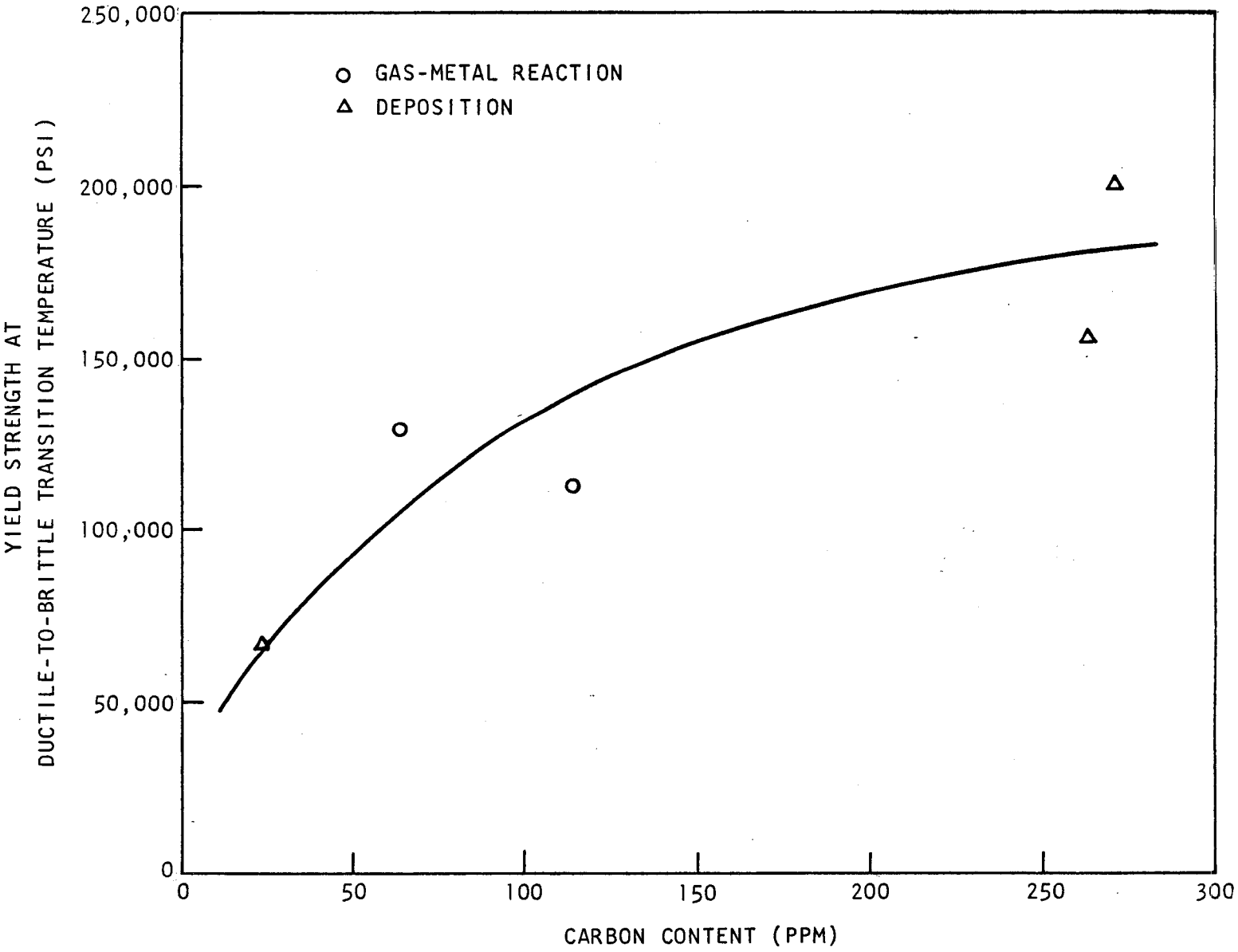


Fig. 3--Yield strength at the DBTT as a function of carbon content

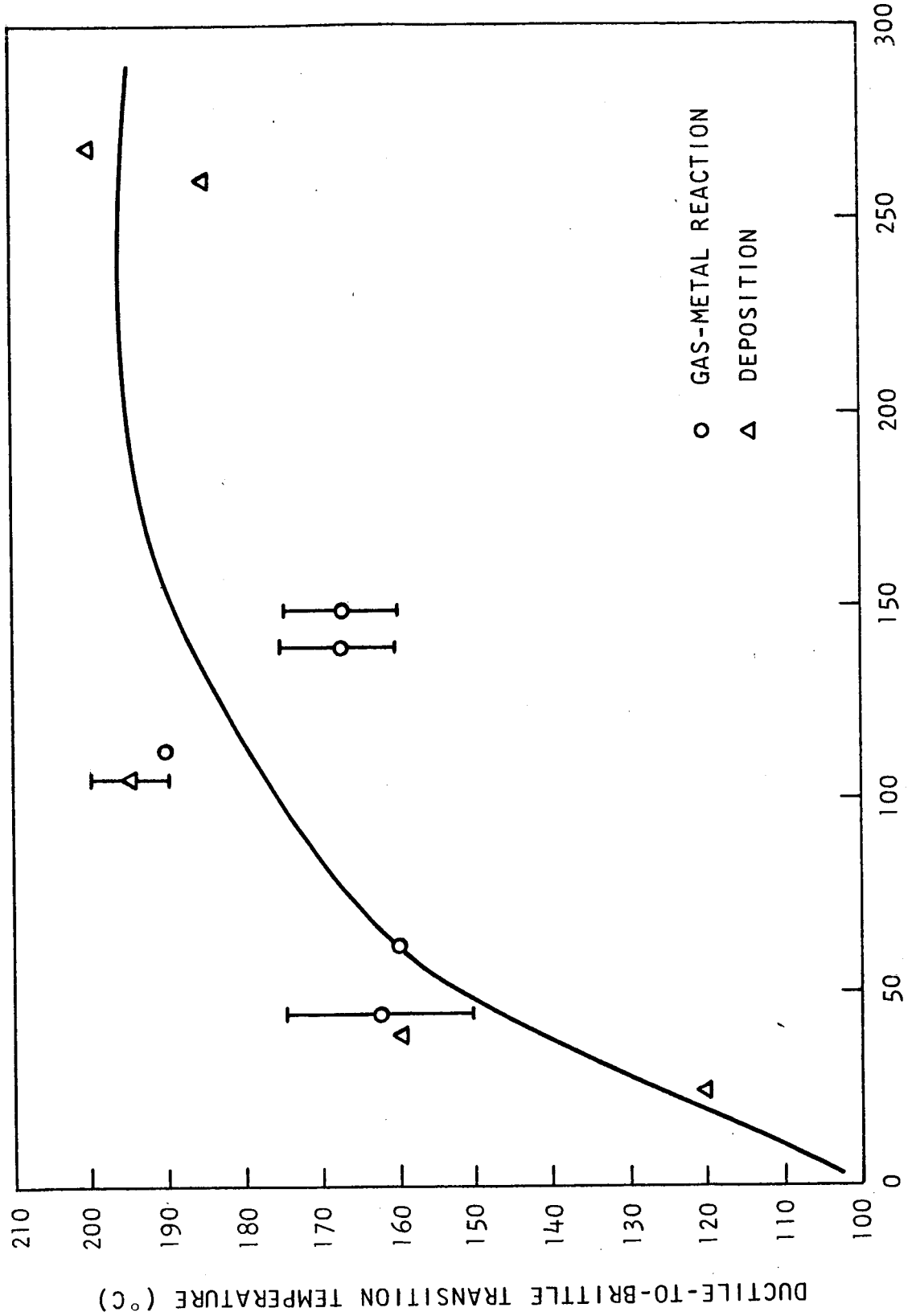


Fig. 4--Ductile-to-brittle transition temperature as a function of carbon content

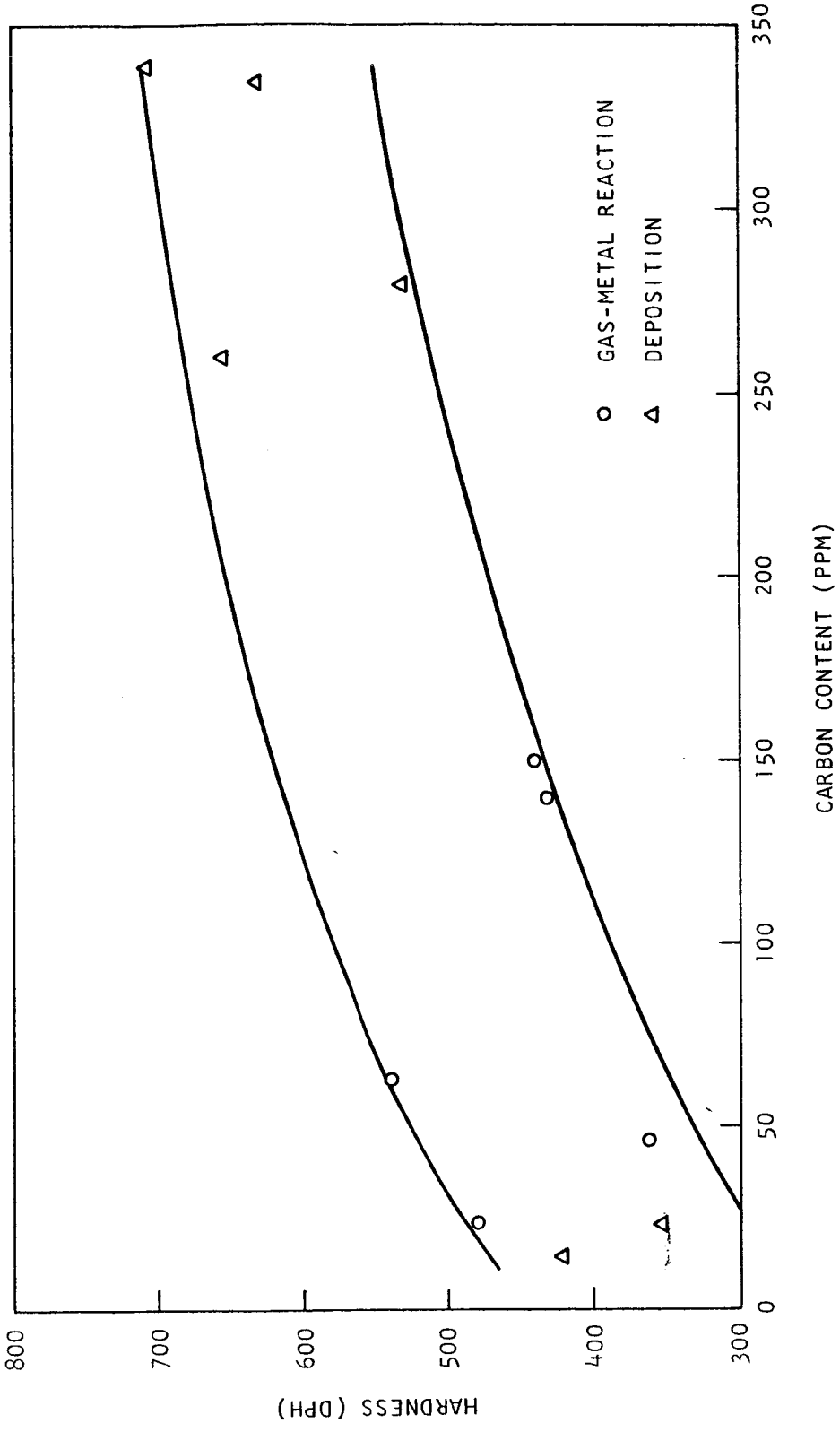


Fig. 5--Hardness as a function of carbon content

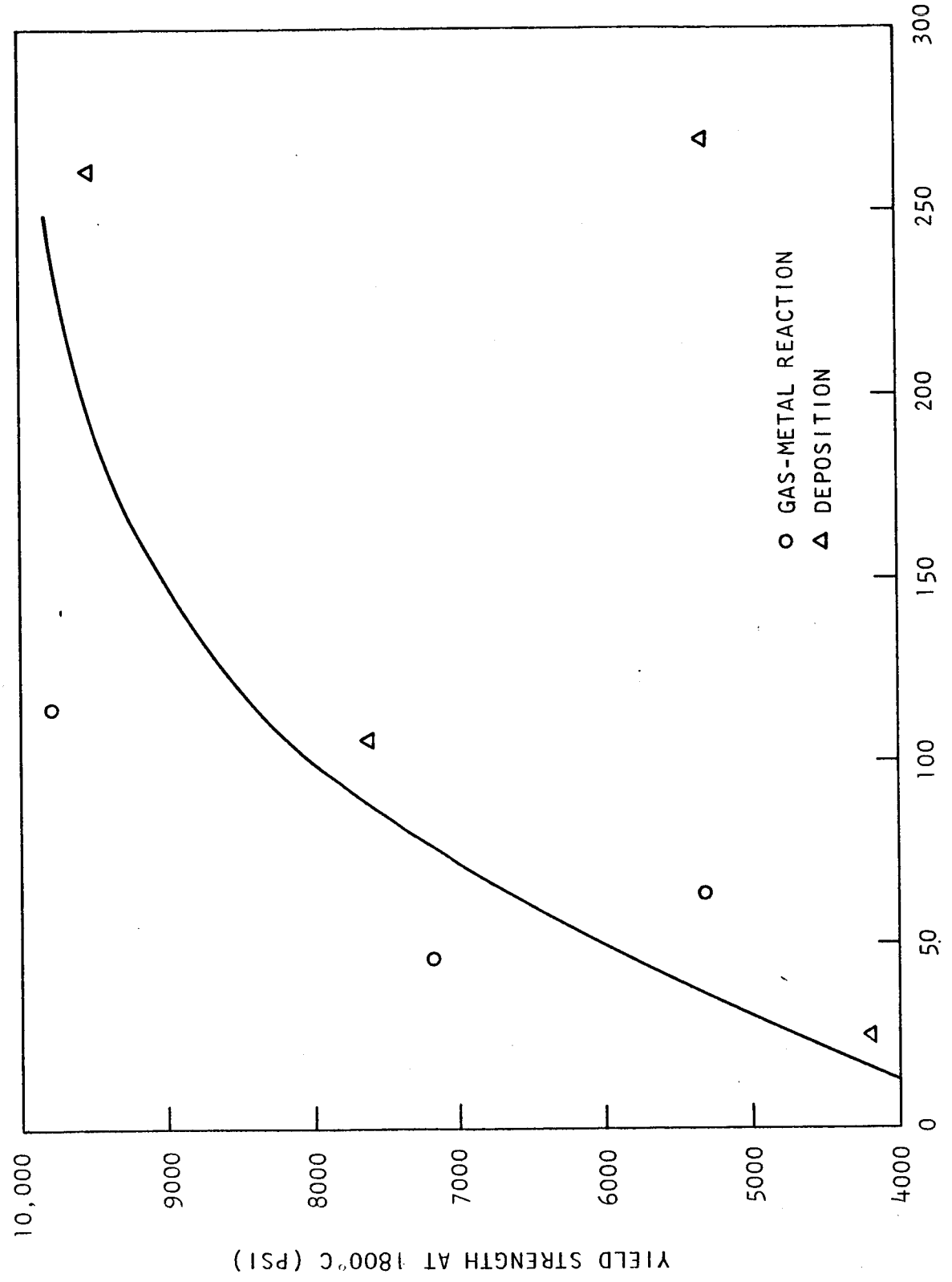
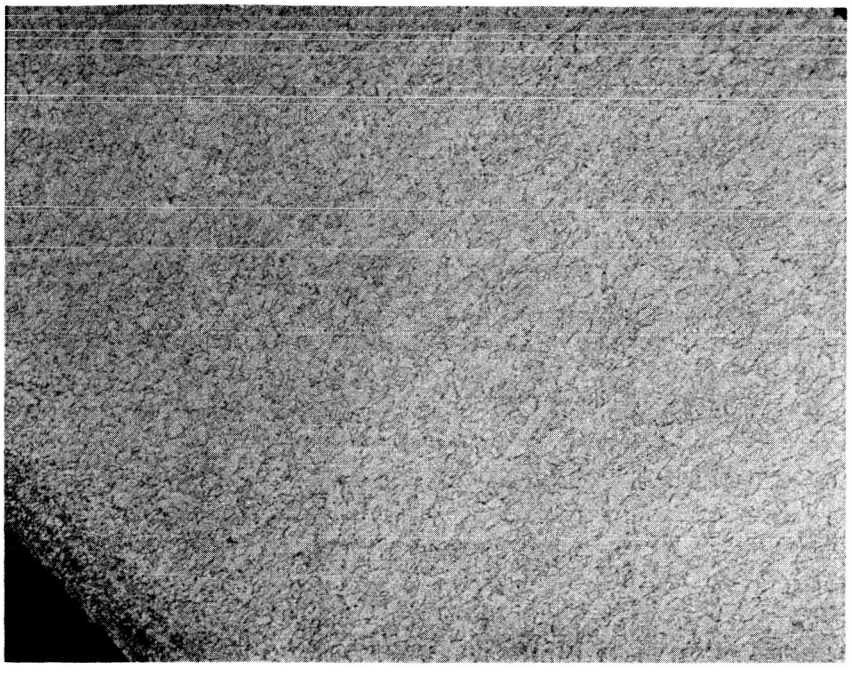
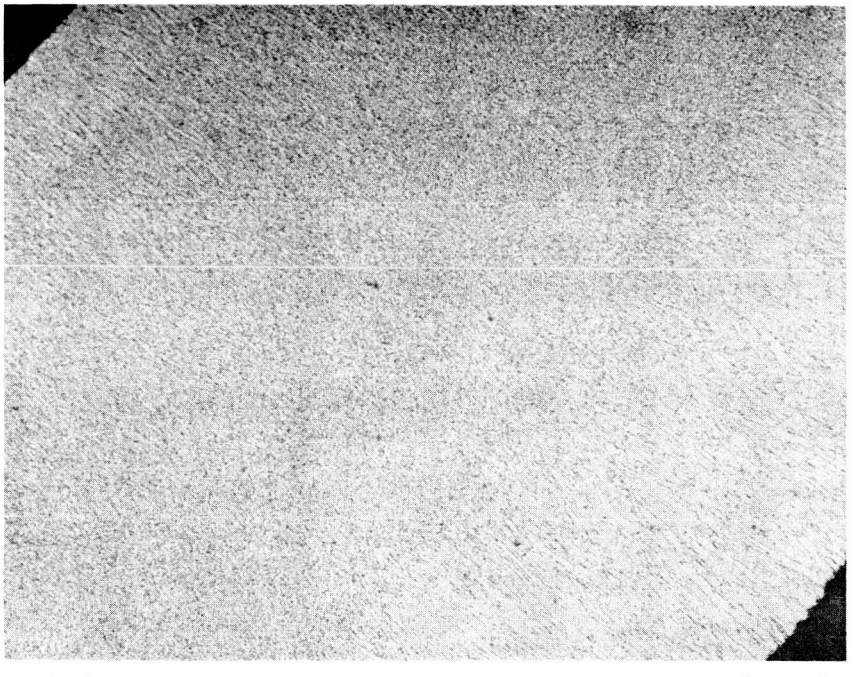


Fig. 6--Yield strength at 1800°C as a function of carbon content



M12858-2 Etched (100X)
(a)



M12856-2 Etched (100X)
(b)

Fig. 7--Vapor-deposited tungsten containing an average of (a) 262 ppm and (b) 270 ppm. Carbon added during deposition from CH_4: WF_6: H_2 volume rates of 1.4:1:3.1 and 2.6:1:2.7, respectively

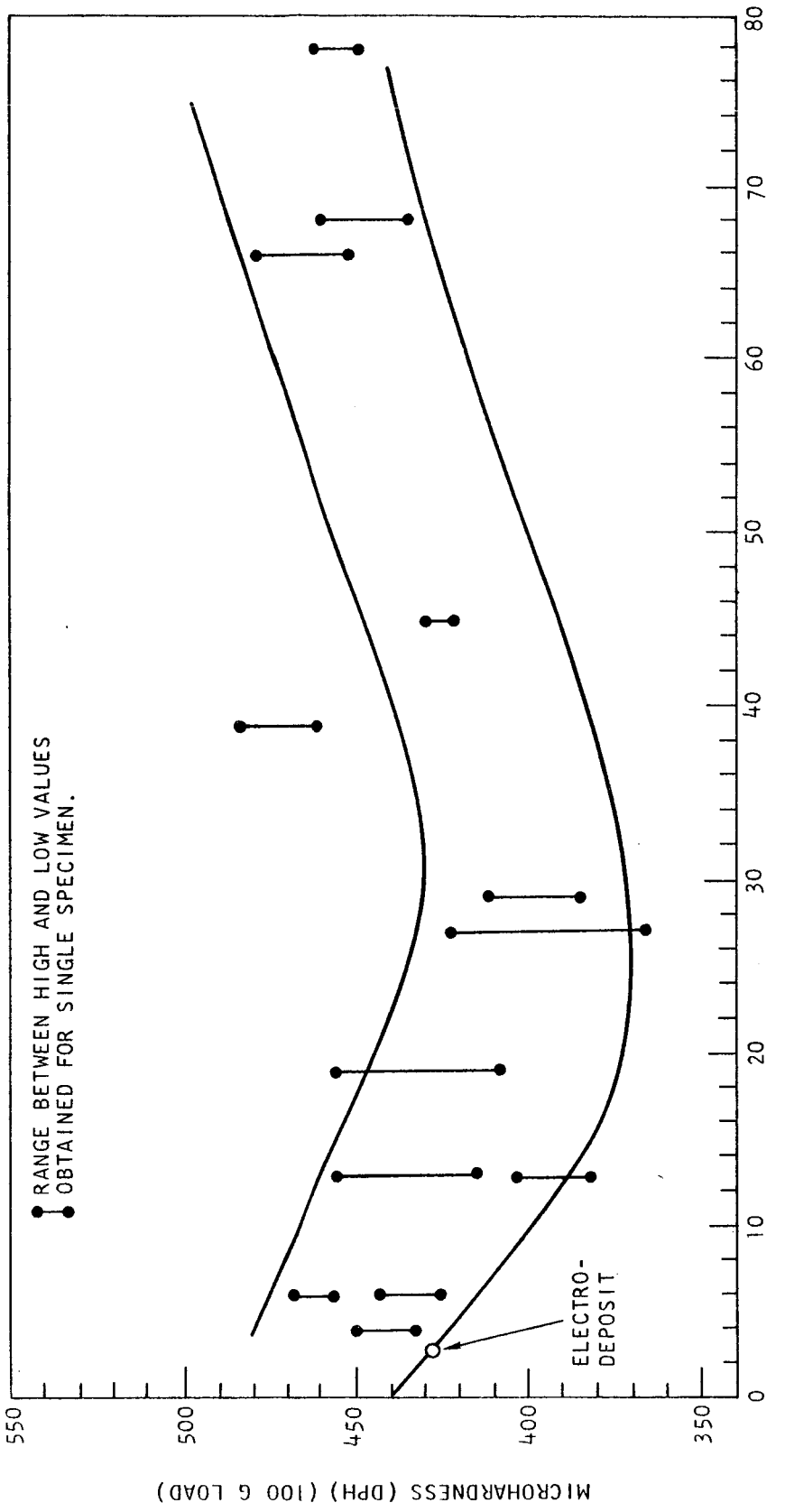


Fig. 8--Hardness versus fluorine content

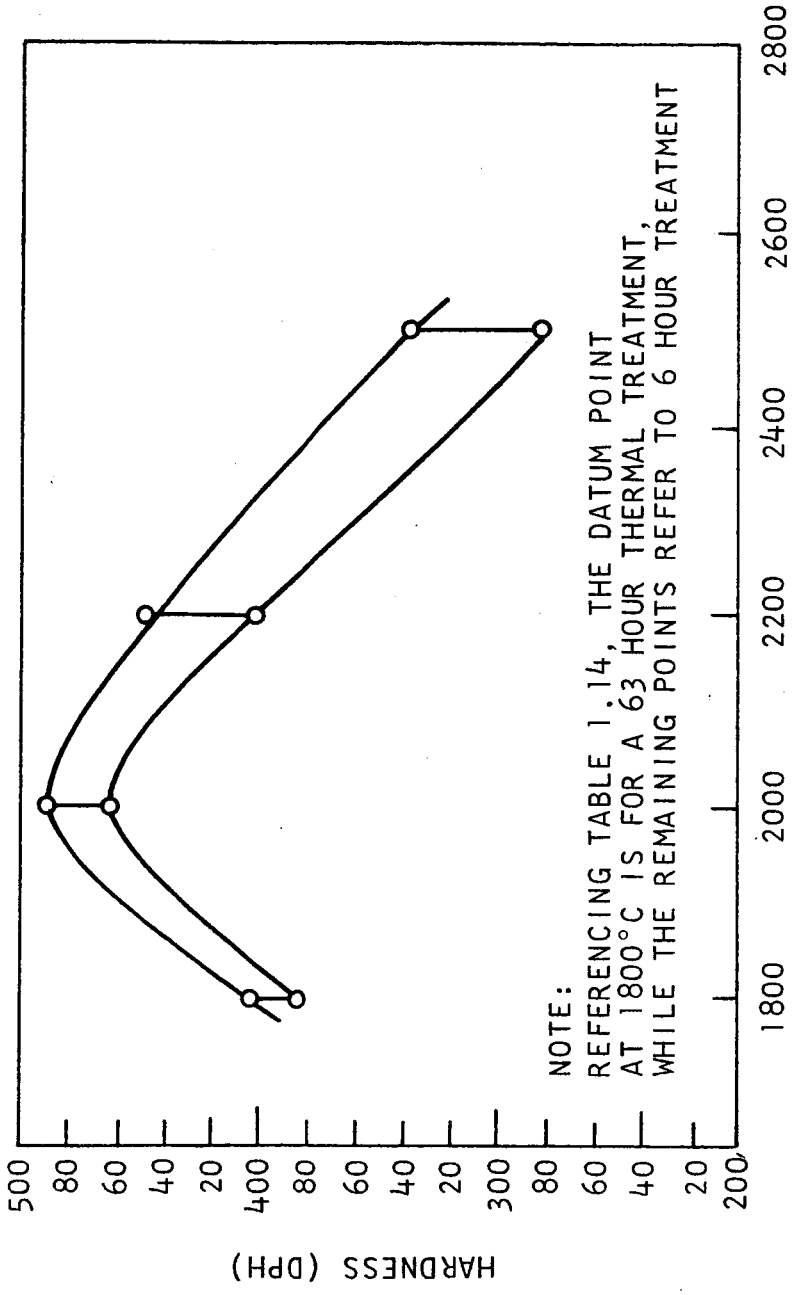


Fig. 9--Effect of thermal treatment on hardness
Specimen ECM-1 having 29 ppm fluorine

It must be noted that the hardness of these specimens was measured after heating slowly to 1800°C and holding this temperature for 1 hour.

b. Ductile-to-Brittle Transition Temperature: A unique relationship between fluorine content and DBTT was not found. The DBTT of specimens having a given fluorine content were found to be quite dependent on their thermal history.

It is not impossible that the fluorine content may still influence the transition temperature through a subtle synergistic interaction with some other impurity in the tungsten, but such an effect has not been discerned.

c. Grain Boundary Porosity: There appears to be a relationship between fluorine content, annealing temperature, annealing time, and the tendency for the formation of grain boundary porosity. Also, there appears to be a threshold temperature ($\sim$ 2100°C) below which no porosity is formed, even in specimens of high fluorine content; but, the critical fluorine content necessary to avoid pore formation at temperatures above this threshold moves to lower values as the temperature is increased.

Fig. 10 summarizes the data obtained for relatively short time thermal treatments. In this plot, the triangles denote those conditions where porosity was not found. Fig. 11 illustrates the type of porosity observed.* Note that the pores do not occupy a large part of the specimen volume and are not interconnected.

Fig. 10 can be divided into two regions where, with one exception, the temperature-fluorine relationships in the lower left portion correspond to no porosity, while the upper right region indicates those conditions associated with porosity. The critical fluorine content dividing these two regions moves toward lower values at the higher temperatures. As one moves toward the lower temperature region, there appears to be a

*By light microscopy.

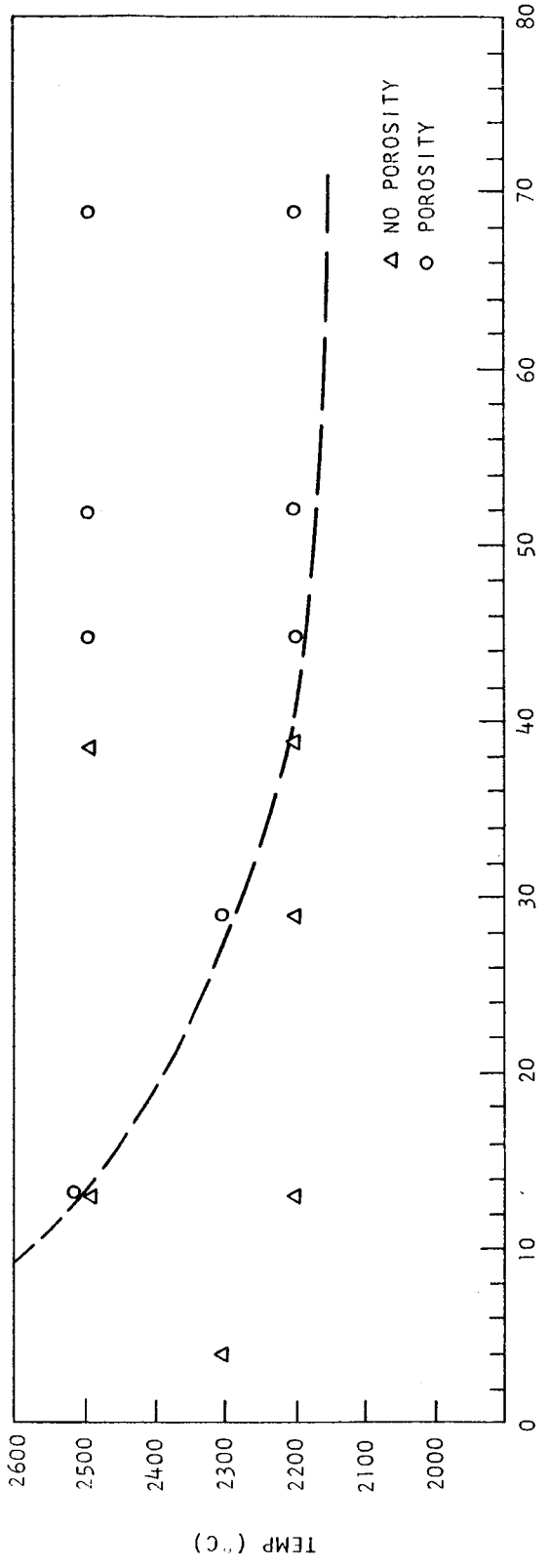
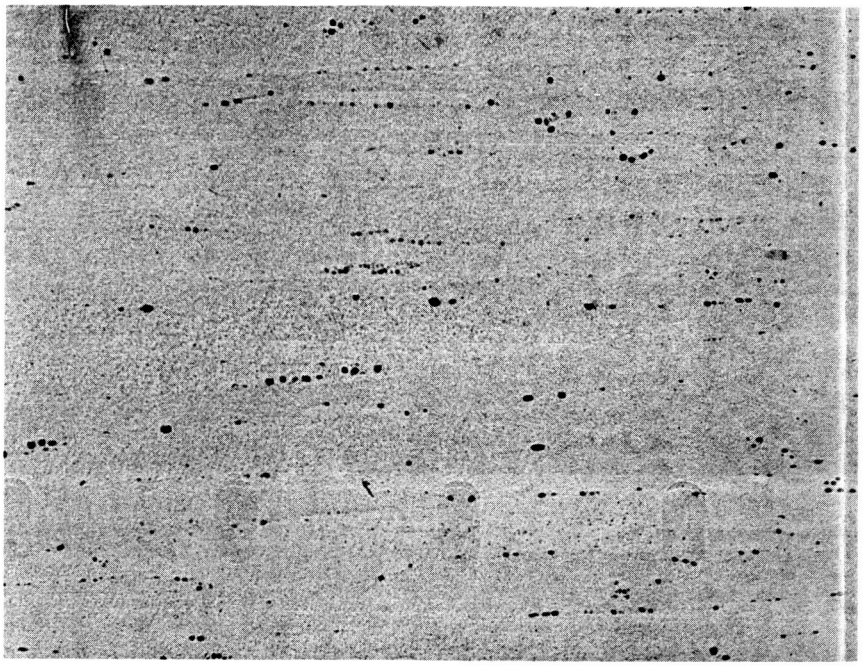


Fig. 10--Relationship between grain boundary porosity, annealing temperature, and fluorine content



M13414-2 (100X)

Fig. 11--Specimen containing 29 ppm fluorine after a six hour anneal at 2300°C

threshold temperature below which very large fluorine contents can be accepted before porosity is observed. It must be noted that more data would be required to firmly establish this; however, no porosity has been observed at temperatures below 2200°C in any specimen made under our reference condition at either General Atomic or San Fernando Laboratories.

While Fig. 10 shows some relationships between fluorine content, temperature, and grain boundary porosity, two additional factors are missing. One is the sensitivity of the detection system employed--it is entirely possible that a more sensitive method of observation such as electron microscopy would detect pore formation in specimens now listed as having no porosity. A second factor is a time coordinate; i.e., it has been observed that, at least at the higher temperature, pore formation has a time dependence. For example, a specimen with 13 ppm fluorine exhibited no porosity after a 2 hour thermal treatment at 2500°C, but porosity was observed when the thermal treatment had been extended to 8.5 hour.

d. Resistance to Grain Growth: At this time, only qualitative observations can be made concerning grain growth as related to fluorine content. If the fluorine content-temperature conditions are such that grain boundary porosity is formed very rapidly, then the pores inhibit grain growth; i.e., in those specimens in which porosity is observed, one does not observe grain growth. Porosity has never been observed in specimens where gross grain growth has occurred. There is still a third possibility; i.e., neither grain growth nor pore formation are observed.

In conclusion, only three conditions have been observed in heat treated vapor-deposited tungsten:

1. Pores are observed--no grain growth.
2. Massive growth--no pore formation.
3. No grain growth--no pore formation.

PROPERTIES OF THERMALLY TREATED VAPOR-DEPOSITED TUNGSTEN

To gain a better understanding of the behavior of vapor-deposited tungsten near its use temperature, the following properties were examined:

1. The resistance of vapor-deposited tungsten, mechanically strained at low temperature, to grain growth during heat treatment.
2. The effect of thermal treatment on the hardness and ductile-to-brittle transition temperature of vapor-deposited tungsten.
3. The effect of cyclic thermal treatments on the grain growth and porosity of vapor-deposited tungsten.
4. The creep-rupture behavior of vapor-deposited tungsten at 1800°C.

Effect of Mechanical Strain on Resistance to Grain Growth

Specimens mechanically strained at temperatures from 175° to 302°C were subsequently heat treated at 2500°C for 2 hours to determine whether grain growth was initiated due to this strain. The temperature at which strain was applied was selected to be that temperature where the vapor-deposited tungsten just begins to show ductility. The 0.5 in. I.D., 0.035 in. wall specimens were deformed 0.055 ± 0.005 in. out of round. An additional $\frac{1}{2}$ in. diameter cylindrical specimen was flattened at 900°C and heat treated at 2500°C for one hour. No grain growth was observed in either the strained or control specimens. However, the formation of grain-boundary porosity may have confused matters by acting as an inhibitor to grain growth.

Effect of Thermal Treatment on the Mechanical Properties of Vapor-Deposited Tungsten

Thermal treatments of 1800° to 2500°C followed by rapid furnace cooling caused the following effects:

1. All heat treatments reduced the hardness values to within a very narrow range 351-401 DPH, independent of prior hardness or heat treatment temperature.
2. The optimum two-hour thermal treatment to attain the maximum reduction in the DBTT was 2200°C. The magnitude of the change in

the DBTT effected by this thermal treatment was dependent upon the initial value. After a 2200°C treatment, all specimens fell in the narrow range, 90° to < 110°C. (See Fig. 12.)

3. If a 2300°C thermal treatment is followed by very slow cooling, the hardness falls in the same range as rapidly cooled specimens, but the transition temperature is not significantly reduced. This is attributed to the presence of a "precipitate" formed during cooling at the grain boundaries. Electron microscopy (Fig. 13) and electron microprobe analysis identified these "precipitates" as tungsten crystals which had formed during deposition. They are not normally observable, but become decorated with impurities during this slow-cooling treatment.

The Effect of Cyclic Thermal Treatment on Grain Growth

Specimens were heated at 2500°C to simulate a reactor transient, and then lowered to 1800° and 2000°C for 100-hour thermal treatments, to see if grain growth once initiated at the higher temperature would continue to grow when the temperature was lowered. As shown in Fig. 14, no continued grain growth was observed, but it was noted that the grain-boundary porosity formed at 2500°C seemed to enlarge somewhat when subsequently held at 2000°C. The lack of continued growth could again be attributed to pinning of the boundaries by the porosity formed during the 2500°C thermal treatment.

Creep Properties

A cylindrical specimen was machined from a slab cut from the wall of a piece of thick-walled vapor-deposited tubing. This specimen was creep tested at Thompson-Ramo-Woolridge under NASA sponsorship. The test conditions were: temperature = 1760°C, stress = 1000 psi. After 664 hours, the strain was 0.715%; and after 2671 hours, the strain was 1.570%. These values were essentially identical to those expected for arc-cast tungsten.[3]

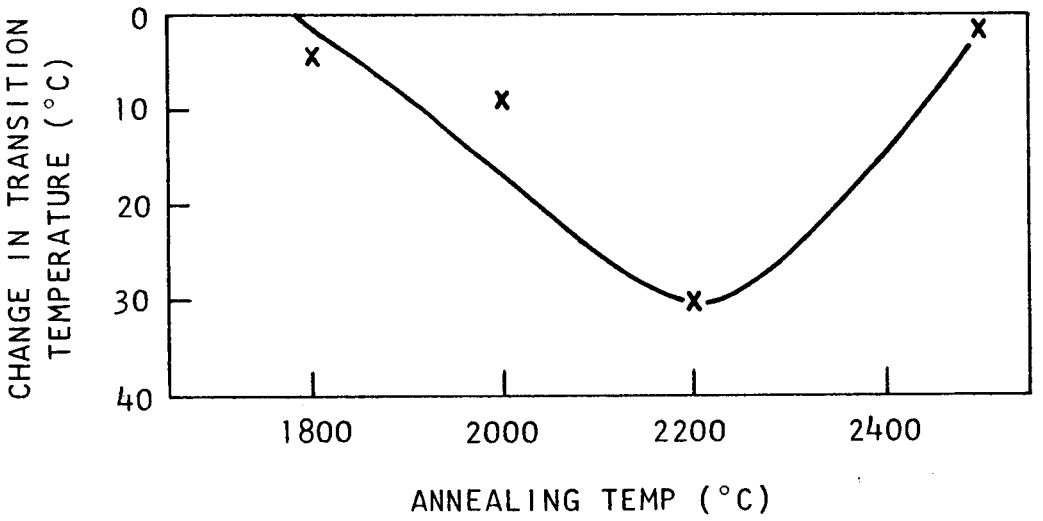
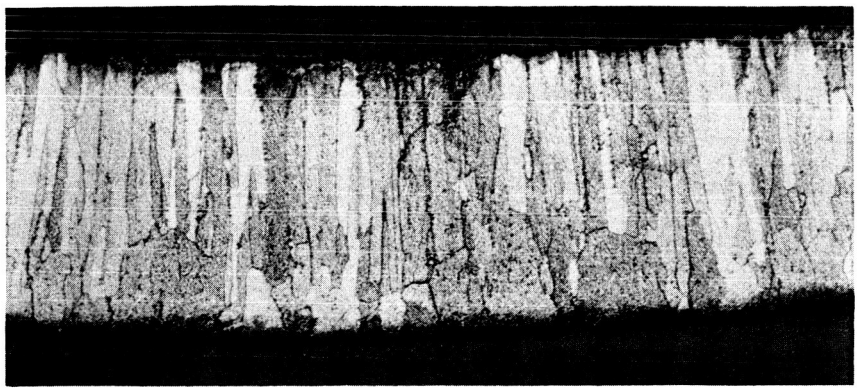


Fig. 12--Effect of thermal treatment on the DBTT of vapor-deposited tungsten

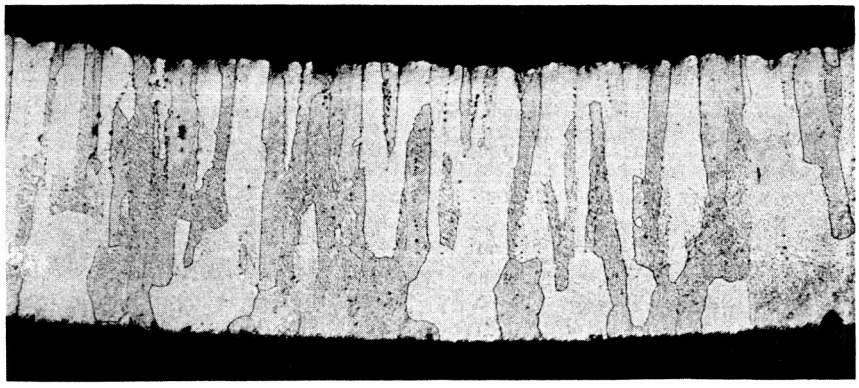
P-6751 (5000X)

Fig. 13--Electron micrograph of grain boundary precipitate on slow cooled tungsten specimen



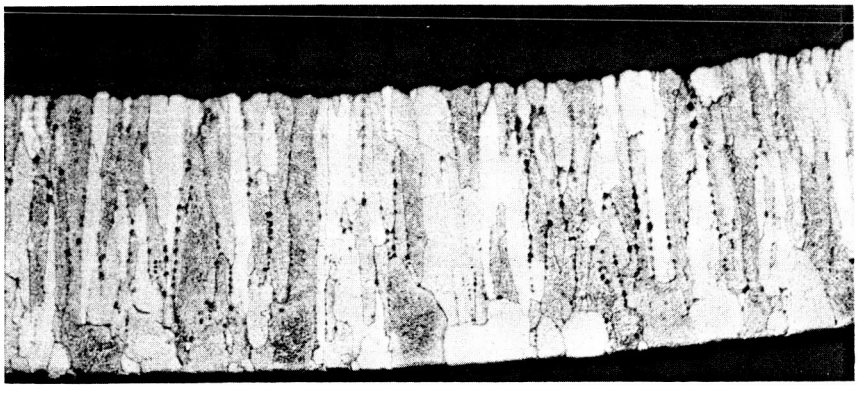
M8578-1 Etched (100X)

(a) Specimen No. 2 heat-treated at 2500°C for 1 hour



M10627-1 Etched (100X)

(b) Same specimen after additional heat treatment at 1800°C for 100 hours



M10753-1 Etched (100X)

(c) Same specimen after additional heat treatment at 2000°C for 100 hours

Fig. 14--Grain growth in vapor-deposited tungsten thermally treated at 2500°C to initiate growth and then held for longer times at lower temperatures. Note that there was no significant increase in grain growth after the initial thermal treatment. Also observe the increase in grain-boundary porosity after the 2000°C treatment.

REFERENCES

1. Weinberg, A. F., J. R. Lindgren, N. B. Elsner, and R. G. Mills, "Suppression of Grain Growth in Vapor-Deposited Tungsten up to 2500°C," Nuclear Applications, Vol. I, p. 581-583, dated 1 December 1965.

2. Mills, R. G., J. R. Lindgren, A. F. Weinberg, "An Evaluation of Vapor-Deposited Tungsten Tubing," NASA-CR-54277, dated October 19, 1964.

3. Schmidt, F. F., and H. R. Ogden, "The Engineering Properties of Tungsten and Tungsten Alloys," DMIC 191, dated September 27, 1963.